AN INVESTIGATION OF ADSORPTION OF MANGANESE (II) ON TO THE CLAY COLLECTED FROM A POND IN TIRUCHIRAPPALLI, INDIA

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ABSTRACT
Adsorption of manganese (II) ions by natural clay was studied by the batch mode technique. The influence of pH, particle size, contact time, initial concentration of the adsorbate and temperature were experimentally verified. The results revealed that the adsorption of manganese (II) by natural clay is exothermic and also proved that the natural clay is effective in adsorption/ion exchange process.

KEYWORDS: Pond clay, adsorption, parameters, isotherm modeling.

1.INTRODUCTION
The existing technologies for waste water treatment have major problems. Costs involved in the construction of waste water treatment plants are un-economical, it consumes lot of space, and commercially they are unattractive and have disposal problems. The technologies are divided into three types namely biological, chemical and physical.[1] Manganese is a very common compound that can be found everywhere on earth. Groundwater is a main source of drinking water and the soluble Mn(II) often exceeds WHO standard. It is present in the atmosphere as suspended particulates resulting from industrial emission, soil erosion, and volcanic emissions.[2] Manganese in particular is considered a pollutant mainly because of its organoleptic properties in high concentrations, it causes neurological disorders and brain damage.[3] In the present work, the adsorption of Mn(II) on the natural clay was studied.
2. EXPERIMENTAL

Natural clay (~500g) from a pond in Uttamarceli, Tiruchirappalli (~ one foot from the surface – during June 2013) was collected, washed well with water (to remove the soluble impurities) and filtered. Then, the material was stirred well with ~1N HNO₃ (to remove the acid – soluble impurities), filtered and washed repeatedly with distilled water (filtrate checked with litmus paper). Then, the clay material was filtered, washed well with double distilled water, dried, sieved to different sizes and kept in airtight glass containers. The clay thus obtained is abbreviated as PC (Pond Clay).

2.1. BATCH EQUILIBRATION METHOD

All experiments were carried out in batch mode. Batch mode was selected because of simplicity and reliability. In many applications, the preliminary evaluation program may take the form of simple feasibility study where capacities of adsorbents for the removal of chosen adsorbates are determined by simple batch experiments in laboratory. This study together with the knowledge of similar operating may provide sufficient capacity and design information to proceed with full scale design. In other cases considerable effort may be required for full scale implementation. Keeping this in view batch experiments were done in different ground joint glass bottles of 100 ml capacity. Prior to each experiment a predetermined amount of absorbent was added to each flask. The stirring was kept constant (100rpm) for each run through to ensure equal mixing. Each bottle was filled with 50ml of sample was withdrawn from the shaker at the predetermined time interval, filtered and the residual concentration of the sample was measured. Concentrations of metal ions before and after adsorption was measured using a photocolorimeter.

All experiments were conducted by following the batch mode adsorption technique in a 100 ml reagent bottles by varying the parameters viz., particle size (<75 µm to 425µm - 500 µm), initial concentration of synthetic Mn²⁺ solution (25 mg/l - 200 mg/l), contact time (5 min - 50 min), pH (3 - 7) and temperature (27°C-47°C). The optimized size for PC was first examined followed by varying contact time, initial concentration, pH and temperature.

The metal ion retained in the adsorbent phase, \( q_e \) (mg/g) was calculated using

\[
q_e = \frac{(C_i - C_e)}{m} \times V
\]

Where \( V = \) Volume (ml) of the equilibrated solution,
m = Mass of the adsorbent (g),

\( C_i \) = Initial concentration of synthetic \( \text{Mn}^{2+} \) solution (mg/l),

\( C_e \) = Mn(II) at equilibrium (mg/l).

The percentage removal (%) of \( \text{Mn}^{2+} \) ions was calculated using the following equation \[4\],

\[
\text{Removal (\%)} = \left( \frac{C_i - C_e}{C_i} \right) \times 100
\]

2.1.1. EFFECT OF ADSORBENT PARTICLE SIZE

Experiments were conducted using PC to evaluate the influence of adsorbent particle size for a constant weight on the removal of manganese ions. The removal of Manganese ions at different particle sizes viz., < 75 µm, 75 µm -150 µm, 150 µm -250 µm, 250 µm -300 µm, 300 µm – 355 µm, 355 µm -425 µm and 425 µm -500 µm were done. The results obtained with the variation of adsorbent particle sizes and the percentage of removal was graphically represented in Fig. 1. The high adsorption efficiency was shown by the particle size of <75 µm. The presence of a large number of smaller particles provides the sorption system with a larger surface area available for manganese ion removal and it also reduces the external mass transfer resistance in addition to ion exchange. \[5\]

![Fig. 1 Variation in % removal of Mn(II) with Particle size](image)

2.1.2. EFFECT OF pH

pH is one of the important factor to be considered in ion exchange/ adsorption process, since in many cases it alters the surface charge on the sorbents. The ion exchange / adsorption of manganese ions onto the sorbent at various pH values (3 - 7) was shown in Fig. 2. Initially the increase in pH value increases the removal capacity. The percentage of the removal
increases from 52.26 % to 93.17 % with the increase in pH from 3 to 6 and then starts decreasing . The reason may be due to the high degree of deprotonation of the functional group on the surface of hydrogel bead that occurs at high value of pH.[6]

![Fig. 2 Variation in % removal of Mn(II) with pH](image)

**2.1.3. EFFECT OF CONTACT TIME**

![Fig. 3 Variation in % removal of Mn(II) with contact time](image)

It was found that the removal of manganese ions increases with increase in contact time to some extent. Further increase in contact time did not increase the percentage of Mn(II) removal. The adsorption increases from 5 min until 50 min as given in Fig. 3 and then decreases. The rate of Mn(II) removal is higher in the beginning due to the larger surface area of the adsorbent being available for the ion exchange/ adsorption of the manganese ions. The adsorption capacity starts decreasing after 35 min due to the desorption of manganese ions from the sorbent material. Surface adsorption and ion exchange can be considered as the driving force of manganese ion removal.[7]
2.1.4. EFFECT OF INITIAL CONCENTRATION OF Mn\textsuperscript{2+} SOLUTION

For an adsorptive process, in the optimized period of contact time (30 min.), the % removal varies directly with the initial concentration of synthetic Mn\textsuperscript{2+} ion solution. The ion exchange/adsorption capacity of PC was systematically studied by varying the initial concentration of manganese ions viz., 25 mg/l, 50 mg/l, 75 mg/l, 100 mg/l, 125 mg/l, 150 mg/l, 175 mg/l and 200 mg/l as given in Fig. 4.

![Fig. 4 Variation in % removal of Mn(II) with initial concentration](image)

The capacity of the adsorbent gets exhausted sharply with increase in the initial concentration of Mn\textsuperscript{2+} ions. Results show that the PC shows maximum removal of 97.56 % at 25 mg/l. The decrease in ion exchange/adsorption capacity with respect to initial concentration of synthetic Mn\textsuperscript{2+} solution may be attributed to a high intermolecular competitiveness to occupy the lower energetic sites left behind.\cite{8}

2.1.5. EFFECT OF TEMPERATURE

Another important factor that greatly influences the ion exchange adsorption process is the temperature. The effect of solution temperature was investigated at 27°C, 32°C, 37°C, 42°C and 47°C. The results summarized in Fig. 5 indicate that the adsorption rate decreased with temperature above 30°C. The result indicates that the low temperature favours the removal of manganese ions by ion exchange/adsorption on to PC is exothermic nature. At high temperatures, the decreasing of removal efficiency may be due to the decrease of the thickness of the boundary layer due to increased tendency of the molecules to escape from the adsorbent surface to the solution phase.
2.1.6. EFFECT OF AGITATION SPEED

The % removal decreases with increase in agitation speed (Fig. 6). This may be due to the domination of desorption with respect to adsorption. The maximum removal of 96.68 % was found at 50 rpm.

2.2 ISOTHERM MODELLING

The abilities of two widely used isotherms viz., the theoretical Langmuir and empirical Freundlich isotherms were used to model the adsorption equilibrium data.

2.2.1. LANGMUIR ADSORPTION ISOTHERM

The formation of a monolayer adsorbate on the adsorbent was represented by the Langmuir isotherm model. Thereby, the Langmuir represents the equilibrium distribution of
metal ions between the solid and liquid phases. The Langmuir isotherm is applicable for monolayer sorption onto a surface containing a finite range of indistinguishable sites. The model assumes uniform energies of sorption onto the surface and no transmigration of adsorbate within the plane of the surface. Based on these assumptions, Langmuir has drawn the subsequent equation

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e}$$

Langmuir sorption parameters were determined by remodelling the equation into linear type.

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e}$$

Where,

$C_e$ = the equilibrium concentration of adsorbate (mg/l)
$q_e$ = the amount of manganese ion adsorbed per gram of the adsorbent at equilibrium (mg/g)
$Q_0$ = maximum monolayer coverage capacity (mg/g)
$K_L$ = Langmuir isotherm constant (l/g)

The values of $Q_0$ and $K_L$ were computed from the slope and intercept of the Langmuir plot of $1/q_e$ versus $1/C_e$ as given in Fig. 7. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter $R_L$, which is a dimensionless constant mentioned as separation factor or equilibrium parameter.

$$R_L = \frac{1}{1 + (1 + K_L C_0)^{-1}}$$

![Fig. 7 Langmuir adsorption isotherm](image)
Where,
\( C_0 \) = initial concentration of Mn\(^{2+} \) solution,
\( K_L \) = the constant associated with the energy of adsorption (Langmuir constant).

\( R_L \) value indicates the nature to be unfavourable if \( R_L > 1 \), linear if \( R_L = 1 \), favourable if \( 0 < R_L < 1 \) and irreversible if \( R_L = 0 \). From this analysis work, the utmost monolayer coverage capability (\( Q_0 \)) from the Langmuir isotherm model was determined to be 0.0005 mg/g, \( K_L \) was 500 ml/g and the separation factor, \( R_L \) was 0.026. The above parameter confirms the ion exchange/adsorption was favourable. The \( R^2 \) value (0.997) proved the fitness of Langmuir isotherm model on ion exchange/adsorption.

2.2.2. FREUNDLICH ADSORPTION ISOTHERM

This isotherm is used to describe the adsorption characteristics for the heterogeneous surface. These data often fit the empirical equation proposed by Freundlich.\(^{10} \)

\[
Q_e = K_f C_e^n
\]

Where \( K_f \) = Freundlich isotherm constant
\( n \) = adsorption intensity
\( C_e \) = the equilibrium concentration of adsorbate
\( Q_e \) = the amount of Mn\(^{2+} \) adsorbed per gram of the adsorbent at equilibrium

![Fig. 8 Freundlich adsorption isotherm](image)

By linearizing the above equation,

\[
\log Q_e = \log K_f + \frac{1}{n} \log C_e
\]
The constant $K_f$ is an approximate indicator of adsorption capacity, while $1/n$ is a function of the strength of adsorption in the adsorption process. If $n = 1$, then the partition between the two phases is independent of the concentration. If the value of $1/n$ is below one it indicates a normal adsorption. On the other hand, $1/n$ being above one indicates cooperative adsorption. The function has an asymptotic maximum as pressure increases without bound. As the temperature increases, the constants $k$ and $n$ change to reflect the empirical observation that the quantity adsorbed rises more slowly and higher pressures are required to saturate the surface. However, $K_f$ and $n$ are the parameters characteristic of the sorbent-sorbate system, which must be determined by data fitting. Specifically, the linear least-square method and the linearly transformed equations have been widely applied to correlate sorption data where $1/n$ is a heterogeneity parameter; the smaller the $1/n$, the greater the expected heterogeneity. This expression reduces to a linear adsorption isotherm when $1/n = 1$. If $n$ lies between one and ten, this indicates a favourable sorption process. The value of $1/n = 0.295$ while $n=3.38$ indicating that the ion exchange/ adsorption was favourable and the $R^2$ value (0.856) indicated the applicability of Freundlich isotherm on to ion exchange/ adsorption.

3. CONCLUSION

From the above study, the optimum condition of various parameters for the manganese adsorption using clay material collected from a pond in Tiruchirappalli was found out. Also the isotherm modeling viz., Langmuir and Freundlich isotherm were studied. Among the two, the Langmuir fitted well when compared to Freundlich which confirms that the ion exchange/ adsorption seems to follow the monolayer formation. Since, the present technique removes the manganese ions from water using natural clay, it can be considered as a green technique.

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REFERENCES


